PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C04B 35/584, 35/599

A1

(11) International Publication Number: WO 97/35817

(43) International Publication Date: 2 October 1997 (02.10.97)

(21) International Application Number: PCT/SE97/00524

(22) International Filing Date: 25 March 1997 (25.03.97)

(30) Priority Data:
9601159-8 25 March 1996 (25.03.96) SE

(71) Applicant *(for all designated States except US)*: SANDVIK AB (publ) [SE/SE]; S-811 81 Sandviken (SE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: COLLIN, Marianne [SE/SE]; Kanslersvägen 28, S-128 38 Skarpnäck (SE). MIKUS, Marian [SE/SE]; Älgrytevägen 226, S-127 30 Skärholmen (SE).

(74) Agents: ÖSTLUND, Alf et al.; Sandvik AB, Patent Dept., S-811 81 Sandviken (SE).

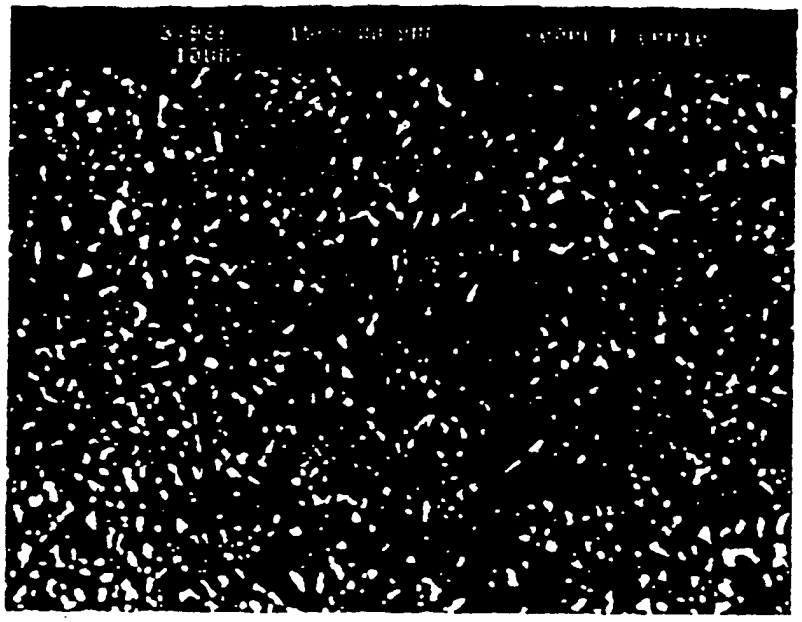
(81) Designated States: JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
*With international search report.*

(54) Title: METHOD OF SINTERING SILICON NITRIDE BASED MATERIALS

(57) Abstract

The present invention relates to a method for sintering of a silicon nitride based material using gas pressure sintering technique. It has been found that using a sintering atmosphere containing nitrogen and 0.1 - 10 vol-% carbon monoxide a cutting tool material is obtained with improved properties, particularly increased edge toughness, when machining heat resistant alloys.



*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | | | TR | Turkey |
| BG | Bulgaria | HU | Hungary | ML | Mali | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MN | Mongolia | UA | Ukraine |
| BR | Brazil | IL | Israel | MR | Mauritania | UG | Uganda |
| BY | Belarus | IS | Iceland | MW | Malawi | US | United States of America |
| CA | Canada | IT | Italy | MX | Mexico | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NE | Niger | VN | Viet Nam |
| CG | Congo | KE | Kenya | NL | Netherlands | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NO | Norway | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | NZ | New Zealand | | |
| CM | Cameroon | | | PL | Poland | | |
| CN | China | KR | Republic of Korea | PT | Portugal | | |
| CU | Cuba | KZ | Kazakstan | R | Romania | | |
| CZ | Czech Republic | LC | Saint Lucia | RU | Russian Federation | | |
| DE | Germany | LI | Liechtenstein | SD | Sudan | | |
| DK | Denmark | LK | Sri Lanka | SE | Sweden | | |
| EE | Estonia | LR | Liberia | SG | Singapore | | |

# Method of sintering silicon nitride based materials

The present invention relates to sintering methods for silicon nitride and sialon material compositions and in particular sialon materials useful for machining of heat resistant alloys.

Silicon nitride is a highly covalent compound with a number of interesting engineering properties. An adverse effect of the strong bonding is a low self diffusivity why the material cannot be consolidated by solid state sintering. Sintering additives such as $Al_2O_3$, $Y_2O_3$ and MgO are used to form a liquid with the $SiO_2$ which is always present on the surface of the $Si_3N_4$ grains. The resulting material has a two-phase microstructure consisting of silicon nitride grains embedded in an intergranular bonding phase, which is normally a glass.

Beta-prime sialon ($Si_{6-z}Al_zO_zN_{8-z}$) is a solid solution where $0<z<4.2$. Sialon materials normally also contain an intergranular bonding phase which can be a glass or contain various crystalline phases. Sialon ceramic cutting tools may also contain alpha sialon ($(Si,Al)_{12}M_x(O,N)_{16}$ where x is between 0.1 and 2 and M can be Li, Ca, Mg, Hf, Zr, Ce, Y, Sc or other lanthanides) and intergranular phases.

Silicon nitride and sialon decompose at high temperatures why sintering normally is performed in nitrogen atmosphere.

Pressureless (atmospheric pressure) sintering, besides nitrogen atmosphere, normally requires embedding of the object to be sintered in a suitable powder bed to avoid decomposition.

Hot isostatic pressing requires encapsulation of the object to be sintered prior to sintering.

Gas pressure sintering (GPS) is a method of sintering powder metallurgical parts to almost 100 %

relative density without any of the precautions necessary for the above mentioned sintering methods. According to this method the first part of the sintering is performed at conventional pressure. When closed porosity is reached the gas pressure is substantially increased and maintained during cooling.

Another advantage of increased pressure during sintering, if nitrogen is used as pressure medium, is a reduction or elimination of the thermal decomposition of the ceramic material.

According to the present invention it has now surprisingly been found that by careful sintering of a silicon nitride based material containing essentially beta sialon in a nitrogen atmosphere in a gas pressure sintering furnace in a sintering cycle comprising addition of carbon monoxide a cutting tool material is obtained with improved properties when cutting heat resistant alloys. The reason to the improvement is not fully understood at present. Since the reduction in porosity is only marginal it is believed that an intergranular phase with favourable properties is obtained and that this fact has a positive influence on the cutting properties particularly edge toughness.

Fig 1 shows in 4000X magnification the microstructure of a Sialon material produced according to the present invention.

The silicon nitride based material according to the present invention is manufactured by powder metallurgical methods i.e. milling a powder mixture comprising $Si_3N_4$, AlN, $Al_2O_3$ and $Y_2O_3$, of which the latter may be replaced partly or completely by other suitable oxides such as oxides from the lanthanide series, in desired proportions followed by pressing and sintering. The mixture is milled for 4 - 48 hours, preferably 6 - 20 hours, in a suitable milling liquid

e.g. propanolic alcohol together with pressing aids, dried and tool pressed to insert blanks of desired geometry. Alternatively, water is used as milling liquid and in this case AlN is replaced with water-resistant AlN or polytype e.g. 21R. The pressing aids are evaporated in a presintering step at 400 - 1000 °C, preferably 500 - 700 °C. The insert blanks are then processed in a gas pressure sintering furnace using a sintering cycle using a sintering atmosphere containing nitrogen 0.1 - 10 vol-%, preferably 0.1 - 1 vol% carbon monoxide. Preferably, carbon monoxide is introduced at a temperature >1500 °C or alternatively during the high pressure part of the sintering process. This makes it possible to increase the oxygen chemical potential during the steps of the sintering cycle where this is favourable. More particularly the sintering process comprises the following steps:

- the first step is heating up to about 1350 °C at subpressure, preferably <0.1 bar,
- the second step is heating to about 1680 °C at 1 bar of nitrogen,
- the third step is increasing the gas pressure to 5 - 50, preferably 5 - 25, most preferably 8 - 20, bar of nitrogen and adding carbon monoxide or, alternatively, using a premixed $CO/N_2$ gas mixture,
- the fourth step is increasing the temperature to the final sintering temperature of 1700 - 1800 °C, preferably 1730 - 1770 °C, and maintaining this gas pressure and temperature for 0.5 - 5 hours, preferably 1 - 3 hours,
- the fifth step is cooling to 1100 °C at maintained gas pressure,
- the sixth step is cooling to room temperature in flowing nitrogen.

The amount of carbon monoxide has to be determined considering the furnace size, total weight and type of silicon nitride based material.

During the fifth step the cooling rate may be increased by further increasing the nitrogen gas pressure.

During the sintering the insert blanks are placed on sintering discs and no powder bed is used. After the sintering the insert blanks are ground into inserts of final shape and dimension.

The method of the present invention can be applied to all kinds of silicon nitride based materials and is not limited to the examples given below. In particular, it applies to sialon material for which particularly good results have been obtained for a material comprising 10 - 20 vol% intergranular phase and rest crystalline sialon grains of which >70 vol-%, preferably >90 vol-%, is beta-sialon with a z-value of 0.5 - 3.0, preferably 1.0 - 2.0 and most preferably 1.0 - 1.5 and up to 10 vol-%, preferably up to 4 vol-%, polytype such as 2H, 8H, 12H, 15R, 21R, 27R, preferably 12H and optionally alpha sialon. The intergranular phase is essentially amorphous i.e. it contains no crystalline phase. The material may further contain small intergranular pores <0.5 µm in size. The material has a microstructure characterized in (see figure 1) elongated beta-sialon grains with a length up 10 µm and with an aspect ratio >5 and smaller sialon grains with a diameter <2 µm, preferably <1 µm, with one or more intergranular phases situated in between the sialon grains.

The method of the invention also applies to a silicon nitride based material containing one or more refractory phases in particular carbides, oxides or nitrides or solid solutions thereof of V, Nb, Ta, Ti, Zr and

Hf. The above mentioned refractory phases may also be in form of whiskers with a small diameter, below 2 μm, preferably below 1 μm. The amount of refractory phases shall exceed 1 vol-% but not exceed 35 vol-%, preferably greater than 5 vol-% but less than 25 vol-%.

Further improvements of the wear resistance of the sialon material according to the invention may be obtained by coating with one or more refractory layers such as $Al_2O_3$, TiC, TiN or Ti(C,N), Ti(C,O), Ti(N,O), Ti(C,N,O) etc using methods known in the art such as CVD, MTCVD, PVD etc. The total thickness of the coating is less than 15 μm, preferably less than 5 μm.

The invention is described with the use of added carbon monoxide. Of course, alternatively other oxygen containing gases e.g. $CO_2$, $O_2$, NO, $NO_2$ can be used alone or in combination with each other and carbon monoxide in such an amount that the corresponding oxygen potential is obtained.

Example 1

A ceramic slurry was manufactured in a conventional way by wet dispersion in propanolic alcohol. The composition of the ceramic raw materials was 5 weight-% of $Y_2O_3$, 8 weight-% of AlN, 24 weight-% of $Al_2O_3$ and balance of $Si_3N_4$. Suitable pressing aids were added. The slurry was dried and sieved through a 0.5 mm sieve and the powder thus obtained was tool pressed to cylindrical insert blanks of the geometry B-RNGN 120800. The insert blanks were then presintered at 600 °C in a hydrogen atmosphere and afterwards divided into two groups and sintered according to two different sintering methods:

Sintering method A (prior art): The insert blanks were sintered in a gas pressure sintering furnace (graphite isolated) in a sintering cycle which first step was heating up to about 1350 °C at subpressure, the

second step was heating to about 1680 °C at 1 bar of nitrogen, the third step was increasing the gas pressure to 12 bar of nitrogen, the fourth step was increasing the temperature to the final sintering temperature of 1750 °C and maintaining the gas pressure and temperature for 2 hours, the fifth step was cooling to 1100 °C at maintained gas pressure, the sixth step was cooling to room temperature in flowing nitrogen. During the sintering the inserts were placed on open sintering discs.

Sintering method B (according to the invention): The insert blanks were sintered in a gas pressure sintering furnace in a sintering cycle which first step was heating up to about 1350 °C at subpressure, the second step was heating to about 1680 °C at 1 bar of nitrogen, the third step was increasing the gas pressure to 12 bar of nitrogen and adding of CO in an amount corresponding to a pressure increase of 0.7 bar, the fourth step was increasing the temperature to the final sintering temperature of 1750 °C and maintaining the gas pressure and temperature for 2 hours, the fifth step was cooling to 1100 °C at maintained gas pressure, the sixth step was cooling to room temperature in flowing nitrogen. During the sintering the inserts were placed on open sintering discs.

The sintered insert blanks were investigated by measuring sintered density and z-value with the following results:

| Sintering method | Sintered density, $g/cm^3$ | z-value |
|---|---|---|
| A (prior art) | 3.165 | 1.97 |
| B (according to the invention) | 3.170 | 1.97 |

The sintered densities received correspond to a relative density of >99%.

Example 2

Insert blanks sintered according to sintering methods A, and B in example 1 were ground to the style RNGN 120700 T01020 and tested in a turning operation developed to evaluate edge toughness. The cutting parameters were as follows:

Workpiece: Inconel 718Å
Cutting speed: 250 m/min
Cutting depth: 0.1 - 6 mm
Feed: 0.15 mm/rev

| Result (mean of four tests): | number of cuts |
|---|---|
| Variant A (prior art): | 9.1 |
| Variant B (according to the invention): | 10.5 |

Example 3

A ceramic slurry was manufactured in a conventional way by wet dispersion in propanolic alcohol. The composition of the ceramic raw materials was 5 weight-% of $Y_2O_3$, 10 weight-% of AlN, 18.3 weight-% of $Al_2O_3$ and balance of $Si_3N_4$. Suitable pressing aids were added. The slurry was dried and sieved through a 0.5 mm sieve and the powder thus obtained was tool pressed to cylindrical insert blanks of the geometry B-RNGN 120800. The insert blanks were then presintered at 600 °C in a hydrogen atmosphere and afterwards sintered according to the invention in a gas pressure sintering furnace (graphite isolated). The first step of the sintering cycle was heating up to about 1350 °C at subpressure, the second step was heating to about 1680 °C at 1 bar of nitrogen, the third step was increasing the gas pressure to 12 bar of nitrogen and adding of CO in an amount corresponding to a pressure increase of 0.5 bar, the fourth step was

increasing the temperature to the final sintering temperature of 1750 °C and maintaining the gas pressure and temperature for 2 hours, the fifth step was cooling to 1100 °C at maintained gas pressure, the sixth step was cooling to room temperature in flowing nitrogen. During the sintering the inserts were placed on open sintering discs.

The sintered insert blanks were investigated by measuring sintered density which was 3.213 g/cm$^3$ and the z-value was z=1.41.

Example 4

A ceramic slurry was manufactured in a conventional way by wet dispersion in water. The composition of the ceramic raw materials was 4.9 weight-% of $Y_2O_3$, 12.8 weight-% of polyphase 21R, 14.5 weight-% of $Al_2O_3$ and balance of $Si_3N_4$. Suitable dispersing and pressing agents were added. The slurry was dried and granulated and the powder thus obtained was tool pressed to cylindrical insert blanks of the geometry B-RNGN 120800. The insert blanks were then presintered at 600 °C in a hydrogen atmosphere and afterwards sintered according to example 3. The sintered insert blanks were investigated by measuring sintered density which was 3.214 g/cm$^3$ and the z-value was z=1.13.

Example 5

A ceramic slurry was manufactured by wet dispersion in water. A water-resistant grade of AlN was chosen and added at the end of the milling step in order to avoid too long exposure to water. The composition of the ceramic raw materials was 5 weight-% of $Y_2O_3$, 10 weight-% of AlN, 18.3 weight-% of $Al_2O_3$ and balance of $Si_3N_4$. Suitable dispersing and pressing agents were added. The slurry was dried and granulated and the powder thus

obtained was tool pressed to cylindrical insert blanks of the geometry B-RNGN 120800. The insert blanks were then presintered and sintered according to example 3.

The sintered insert blanks were investigated by measuring sintered density which was 3.211 g/cm$^3$ and the z-value was z=1.41.

Example 6

Insert blanks sintered according to example 3,4 and 5 were ground to the style RNGN 120700 T01020 and tested in a turning operation developed to evaluate edge toughness. The cutting parameters were as follows:

| | |
|---|---|
| Workpiece: | Inconel 718Å |
| Cutting speed: | 250 m/min |
| Cutting depth: | 0.1 - 6 mm |
| Feed: | 0.15 mm/rev |

| Result (mean of four tests): | number of cuts |
|---|---|
| Example 3 (AlN) | 10.1 |
| Example 4 (polyphase 21R) | 11.0 |
| Example 5 (water-resistant AlN) | 10.5 |

Claims

1. A method for sintering of a silicon nitride based material using gas pressure sintering process consisting of a low pressure sintering step followed by a high pressure sintering step c h a r a c t e r i s e d in using a sintering atmosphere containing nitrogen and 0.1 - 10 vol-%, preferably 0.1 - 1 vol%, carbon monoxide or other oxygen containing gas or gas mixture in such an amount that the corresponding oxygen potential is obtained.

2. A method according to claim 1 c h a r a c t e r i s e d in that only nitrogen and carbon monoxide is used.

3. A method according to claim 2 c h a r a c t e r i s e d in that carbon monoxide is introduced at a temperature >1500 °C.

4. A method according to claim 2 c h a r a c t e r i s e d in that carbon monoxide is introduced during the high pressure step of the sintering process.

5. A method according to claim 3 c h a r a c t e r i s e d in a sintering cycle comprising the following steps

- heating up to about 1350 °C at a subpressure, preferably <0.1 bar,
- heating to about 1680 °C at 1 bar of nitrogen,
- increasing the gas pressure to 5 - 50, preferably 5 - 25, most preferably 8 - 20, bar and adding carbon monoxide,
- increasing the temperature to the final sintering temperature of 1700 - 1800 °C, preferably 1730 - 1770 °C, and maintaining this gas pressure and temperature for 0.5 - 5 hours, preferably 1 - 3 hours,
- cooling to room temperature

6. A method according to claim 1 or 2 characterised in that the silicon nitride based material is sialon.

7. A method according to claim 3 characterised in a sialon material comprising 10 - 20 vol% essentially amorphous intergranular phase, >70 vol-%, preferably >90 vol-%, beta-sialon with a z-value of 0.5 - 3.0 preferably 1.0 - 2.0 and most preferably 1.0 - 1.5 and up to 10 vol-%, preferably up to 4 vol-%, polytype such as 2H, 8H, 12H, 15R, 21R, 27R, preferably 12H and optionally alpha sialon.

8. A method according to any of the previous claims characterised in that the silicon nitride based material contains one or more refractory phases in particular carbides, oxides or nitrides or solid solutions thereof of V, Nb, Ta, Ti, Zr and Hf in the form of particles or whiskers with a small diameter, below 2 µm, preferably below 1 µm whereby the amount of said refractory phases shall be 1 - 35 vol-%, preferably 5 - 25 vol-%.

9. A method according to any of the previous claims characterised in applying a coating of one or more refractory layers such as $Al_2O_3$, TiC, TiN or Ti(C,N) Ti(C,N), Ti(C,O), Ti(N,O), Ti(C,N,O) etc using methods known in the art such as CVD, MT-CVD, PVD etc.

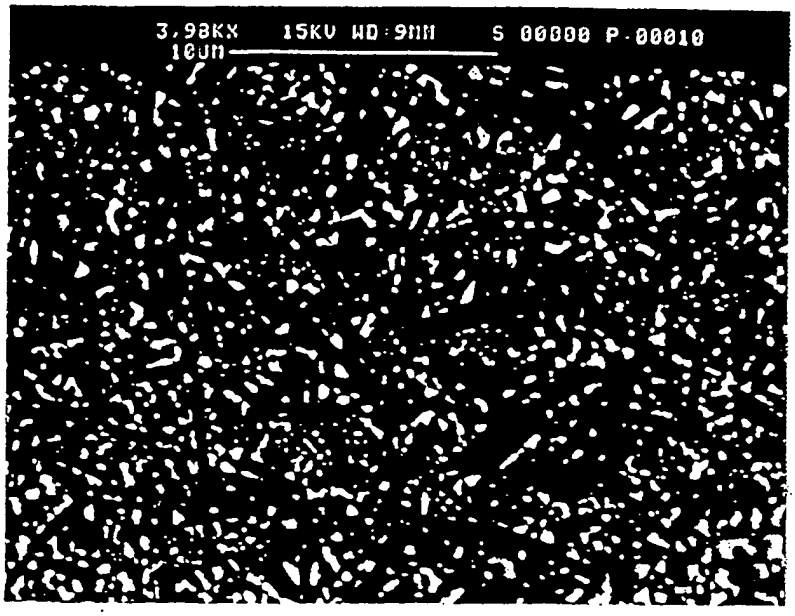



Fig. 1

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 97/00524

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C04B 35/584, C04B 35/599
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | DE 4311155 A1 (MAX-PLANCK-GESELLSCHAFT ZUR FÖRDERUNG DER WISSENSCHAFTEN EV), 6 October 1994 (06.10.94), page 2, line 33 - line 40 | 1-4 |
| A | -- | 1-9 |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" erlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 June 1997 | 08 -07- 1997 |
| Name and mailing address of the ISA/<br>Swedish Patent Office<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile No. +46 8 666 02 86 | Authorized officer<br>May Hallne<br>Telephone No. +46 8 782 25 00 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

03/06/97

International application No.
PCT/SE 97/00524

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| DE 4311155 A1 | 06/10/94 | NONE | |